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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF:

Kazuyuki HAYASHI ET AL.

SERIAL NO. 10/055,809

GROUP ART UNIT: 1773

FILED: August, 10, 2000

EXAMINER: S.A. RESAN

FOR: MAGNETIC RECORDING MEDIUM,
NON-MAGNETIC ACICULAR BLACK
IRON-BASED COMPOSITE PARTICLES
AND PROCESS FOR PRODUCING
THE PARTICLES

DECLARATION UNDER 37 C.F.R. 1.132

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SIR:

Now comes Kazuyuki HAYASHI, a citizen of Japan, and a resident of 34-43-20, Kawauchi 6-chome, Asaminami-ku, Hiroshima-shi, Hiroshima-ken, Japan, who declares and says that:

1. I graduated from Faculty of Engineering, Osaka Prefecture University in March, 1982; received a master's degree from the graduate school of the same university in March 1984.

2. I am currently employed by TODA KOGYO CORPORATION since 1984.

3. I am familiar with the work related to U.S. Patent Application, Serial No. 10/055,809, and am a co-inventor of each and all of U.S. Patents: No. 5,604,015; No. 5,693,690;

No. 5,750,250; No. 6,042,937; No. 6,054,201; No. 6,063,490;
No. 6,130,017; No. 6,248,437; No. 6,287,668; No. 6,416,864;
No. 6,420,030; and No. 6,531,211.

4. I have read the Office Action dated February 13, 2003, have understand the Examiner's rejection to the invention claimed in the above application, have studied US Patent No. 5,750,250 and have ascertained the following.

5. Under my control and supervision the following experiments were conducted:

Experiment 1 (Examples 1 of US Patent No. 5,750,250)

<Production of acicular hematite particles>

750 g of acicular goethite particles (average major axial diameter: 0.220 μm , average minor axial diameter: 0.0275 μm , aspect ratio: 8.00:1, BET specific surface area: 125 m^2/g , content of soluble sodium salt: 452 ppm (calculated as Na), content of soluble sulfate: 283 ppm (calculated as SO_4), pH: 7.1, geometrical standard deviation: 1.27) was suspended in water so as to obtain a slurry, and the concentration of the solid content was adjusted to 5 g/litre. 150 litre of the slurry was heated to 60°C and the pH was adjusted to 9.0 by adding a 0.1-N aqueous NaOH solution.

To the alkali slurry was gradually added 22.5 g of water glass #3, and after the end of addition, the resultant mixture was aged for 60 minutes. The pH of the

slurry was then adjusted to 6.0 by adding a 0.1-N acetic acid solution. Thereafter, the particles were filtered out, washed with water, dried and pulverized by an ordinary method, thereby producing acicular goethite particles coated with a silicon oxide. The SiO_2 content in the acicular goethite particles was 0.86 wt%.

700 g of the acicular goethite particles obtained were charged into a stainless steel rotary furnace, and heat-treated in the air at 300°C for 60 minutes while rotating the furnace, and dehydrated to obtain low-density acicular hematite particles. The thus-obtained low-density acicular hematite particles had an average major axial diameter of $0.150\text{ }\mu\text{m}$, an average minor axial diameter of $0.0216\text{ }\mu\text{m}$, and an aspect ratio of 6.94:1. The BET specific surface area (S_{BET}) was $157.6\text{ m}^2/\text{g}$, the degree of densification ($S_{\text{BET}}/S_{\text{TEM}}$) was 4.13. The content of soluble sodium salt of the goethite particles was 1183 ppm (calculated as Na) and the content of soluble sulfate was 1735 ppm (calculated as SO_4). The pH of the goethite particles was 6.3 and the geometrical standard deviation of the goethite particles was 1.32.

650g of the obtained low-density acicular hematite particles were then charged into a ceramic rotary furnace, and heat-treated in the air at 650°C for 10 minutes while rotating the furnace to seal-treat dehydration pores. The thus-obtained high-density acicular hematite particles had

an average major axial diameter of 0.148 μm , an average minor axial diameter of 0.0217 μm , and an aspect ratio of 6.82:1. The BET specific surface area (S_{BET}) was 53.1 m^2/g , the degree of densification ($S_{\text{BET}}/S_{\text{TEM}}$) was 1.40. The content of soluble sodium salt of the hematite particles was 1386 ppm (calculated as Na) and the content of soluble sulfate was 2739 ppm (calculated as SO_4). The pH was 5.6 and the geometrical standard deviation of the hematite particles was 1.34. The SiO_2 content in the hematite particles was 0.95 wt%.

After 600 g of the high-density hematite particles obtained were roughly pulverized by a Nara mill in advance, they were charged into 3.5 litre of purified water and peptized by a homomixer (manufactured by Tokushu-Kika Kogyo Co., Ltd.) for 60 minutes.

The obtained slurry of the high-density acicular hematite particles was then mixed and dispersed at an axial rotation frequency of 2000 rpm while being circulated by a horizontal SGM (Dispermat SL, manufactured by S.C. Adichem, Co., Ltd.). The acicular hematite particles in the slurry remaining on a 325 mesh sieve (sieve opening: 44 μm) was 0%.

The concentration of the high-density hematite particles in the slurry was adjusted to 100g/litre, and 5 litre of the slurry was adjusted to pH 13.5 by adding 6N-aqueous NaOH solution. The resulting slurry was then heated to 95°C under stirring, and was held for 3 hours at 95°C.

The resultant slurry was then washed with water by a decantation method and the pH of the slurry was adjusted to 10.5. The concentration of the slurry at this point was 96 g/litre.

The particles were filtered out through a Buchner filter, and the purified water was passed into the filtrate until the electric conductivity of the filtrate became not more than 30 μ s. The particles were then dried by an ordinary method and pulverized to obtain the target acicular hematite particles. The acicular hematite particles obtained had an average major axial diameter of not more than 0.148 μ m, a minor axial diameter of 0.0220 μ m, and a specific ratio of 6.73:1. The geometric standard deviation σ_g of particle size (major axial diameter) was 1.33, the BET specific surface (S_{BET}) was 52.5 m²/g, the degree $S_{\text{BET}}/S_{\text{TEM}}$ of densification was 1.40 and the pH was 9.2. They contained 144 ppm of soluble sodium salt (calculated as Na) and 20 ppm of soluble sulfate (calculated as SO₄).

In order to compare the properties under the same criterion, the magnetic recording medium was prepared using the acicular hematite particles obtained in the above, according to the method described in Examples 2 and 3 of our invention, as set forth below.

<Production of a non-magnetic undercoat layer>

12 g of the non-magnetic acicular black iron-based composite particles obtained in Example 1 were mixed with a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone, and each of the obtained mixtures (solid content: 72 % by weight) was kneaded by a plast-mill for 30 minutes.

Each of the thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mm ϕ glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the obtained mixture was mixed and dispersed by a paint shaker for 6 hours. Thereafter, the lubricant was added to the resultant mixture, and the obtained mixture was mixed and dispersed by a paint shaker for 15 minutes to obtain a non-magnetic coating composition.

The thus-obtained non-magnetic coating composition containing the non-magnetic acicular black iron-based composite particles was as follows:

Non-magnetic acicular black iron-based composite particles	100 parts by weight
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Vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group	10 parts by weight
Polyurethane resin having a sodium sulfonate group	10 parts by weight
Lubricant (myristic acid: butyl stearate = 1 : 2)	2.0 parts by weight
Cyclohexanone	56.9 parts by weight
Methylethyl ketone	142.3 parts by weight
Toluene	85.4 parts by weight

The viscosity of the obtained non-magnetic coating composition was 374 cP.

The non-magnetic coating composition obtained was applied to a polyethylene terephthalate film of 12 μm thick to a thickness of 55 μm by an applicator, and the coating film was then dried, thereby forming a non-magnetic undercoat layer. The thickness of the non-magnetic undercoat layer was 3.5 μm .

<Production of a magnetic recording medium>

12 g of magnetic acicular metal particles containing iron as a main component (average major axis diameter: 0.131 μm , average minor axis diameter: 0.0180 μm , aspect ratio: 7.3:1, BET specific surface area value: 58.0 m^2/g , geometrical standard deviation of major axis diameter: 1.40, coercive force: 156.9 kA/m (1972 Oe), saturation

magnetization: $135.0 \text{ Am}^2/\text{kg}$ (135.0 emu/g), Al content: 2.56 % by weight and Co content: 5.85 % by weight), 1.2 g of a polishing agent (AKP-50: trade name, produced by SUMITOMO CHEMICAL CO., LTD.), 0.12 g of carbon black (#3250B, trade name, produced by MITSUBISHI CHEMICAL CORP.), a binder resin solution (30 % by weight of vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group and 70 % by weight of cyclohexanone) and cyclohexanone were mixed to obtain a mixture (solid content: 78 % by weight). The mixture was further kneaded by a plast-mill for 30 minutes to obtain a kneaded material.

The thus-obtained kneaded material was charged into a 140 ml-glass bottle together with 95 g of 1.5 mm ϕ glass beads, a binder resin solution (30 % by weight of polyurethane resin having a sodium sulfonate group and 70 % by weight of a solvent (methyl ethyl ketone : toluene = 1 : 1)), cyclohexanone, methyl ethyl ketone and toluene, and the mixture was mixed and dispersed by a paint shaker for 6 hours. Then, the lubricant and hardening agent were added to the mixture, and the resultant mixture was mixed and dispersed by a paint shaker for 15 minutes.

The thus-obtained magnetic coating composition was as follows:

Magnetic acicular metal	
particles containing iron as a	
main component	100 parts by weight

Vinyl chloride-vinyl acetate copolymer resin having a sodium sulfonate group	10 parts by weight
Polyurethane resin having a sodium sulfonate group	10 parts by weight
Polishing agent (AKP-30)	10 parts by weight
Carbon black (#3250B)	1.0 parts by weight
Lubricant (myristic acid: butyl stearate = 1 : 2)	3.0 parts by weight
Hardening agent (polyisocyanate)	5.0 parts by weight
Cyclohexanone	65.8 parts by weight
Methyl ethyl ketone	164.5 parts by weight
Toluene	98.7 parts by weight

The viscosity of the obtained magnetic coating composition was 7,680 cP.

The magnetic coating composition obtained was applied to the non-magnetic undercoat layer obtained in Example 1 to a thickness of 15 μm by an applicator, and the magnetic recording medium obtained was oriented and dried in a magnetic field, and then calendered. The magnetic recording medium was then subjected to a curing reaction at 60°C for 24 hours, and thereafter slit into a width of 1.27 cm (0.5 inch), thereby obtaining a magnetic tape. The thickness of the respective magnetic recording layer was 1.0 μm .

The properties in the particles were measured by the following methods.

(1) The average major axis diameter, average minor axis diameter and average particle size of particles were respectively expressed by average values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph ($\times 30,000$) by four times in each of the longitudinal and transverse directions.

(2) The aspect ratio of the particles was expressed by a ratio of average major axis diameter to minor axis diameter thereof.

(3) The geometrical standard deviation of particle sizes was expressed by values obtained by the following method. That is, the particle sizes were measured from the above-magnified photograph. The actual particle sizes and the number of the particles were obtained from the calculation on the basis of the measured values. On a logarithmic normal probability paper, the particle sizes were plotted at regular intervals on the abscissa-axis and the accumulative number of particles belonging to each interval of the particle sizes were plotted by percentage on the ordinate-axis by a statistical technique. The particle sizes corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph,

and the geometrical standard deviation was measured from the following formula:

Geometrical standard deviation =

$$\frac{\{\text{particle size corresponding to 84.13 \% under integration sieve}\}}{\{\text{particle size (geometrical average diameter) corresponding to 50 \% under integration sieve}\}}$$

The more the geometrical standard deviation nears 1.0, the more excellent the particle size distribution of the particles.

(4) The specific surface area was expressed by values measured by a BET method.

(5) The volume resistivity of the acicular hematite particles, the acicular iron oxide hydroxide particles and the non-magnetic acicular black iron-based composite particles were measured as follows. First, 0.5 g of the respective particles were weighed, and pressure-molded into a cylindrical shape at 1.372×10^7 Pa (140 Kg/cm²) using a KBr tablet machine (manufactured by SIMAZU SEISAKUSHO CO., LTD.), thereby producing a cylindrical sample to be measured.

The thus-produced sample was then exposed to an atmosphere kept at a temperature of 25°C and a relative humidity of 60%, for not less than 12 hours. Thereafter, the sample was fixed between stainless steel electrodes,

and a voltage of 15V was applied to the sample using a Wheatstone bridge (TYPE2768, manufactured by YOKOGAWA-HOKUSHIN DENKI CO., LTD.), thereby measuring a resistance value R (Ω) of the sample.

Next, an upper surface area A (cm^2) and a thickness t_0 (cm) of the cylindrical sample were measured, and the respective measured values were substituted for A and t_0 of the following formula to obtain the volume resistivity ($\Omega \cdot \text{cm}$) of the sample.

$$\text{Volume resistivity } (\Omega \cdot \text{cm}) = R \times (A/t_0)$$

(6) The myristic acid absorption was measured by the following method. The lower the myristic acid absorption, the more the fatty acid becomes to ooze on the surface of the magnetic recording layer and the lower the friction coefficient thereof.

100 g of 1.5 mm ϕ glass beads, 9 g of particles to be measured and 45 ml of a tetrahydrofuran solution containing myristic acid in an amount enough to form one layer thereof on each particle, were charged into a 140-ml glass bottle, and then mixed and dispersed together for 60 minutes using a paint shaker.

Next, the thus obtained dispersion was taken out, charged into a 50-ml precipitation tube and centrifuged at 10,000 rpm for 15 minutes, thereby separating a solvent portion from a solid portion. The amount (concentration) of

myristic acid contained in the solvent portion was determined by a gravimetric method. By subtracting the measured value from an amount of myristic acid initially charged, the amount of myristic acid contained in the solid portion was obtained as a myristic acid absorption (mg/m^2) of the particles to be measured.

(7) The viscosity of the coating composition was obtained by measuring the viscosity of the coating composition at 25°C at a shear rate D of 1.92 sec^{-1} by using "E type viscometer EMD-R" (manufactured by TOKYO KEIKI, CO., LTD.).

(8) The gloss of the surface of the coating film of each of the non-magnetic undercoat layer and the magnetic recording layer was measured at an angle of incidence of 45° by "glossmeter UGV-5D" (manufactured by SUGA SHIKENKI, CO., LTD.).

(9) The surface roughness R_a is expressed by the center-line average roughness of the surface of the coating film by using "Surfcom-575A" (manufactured by TOKYO SEIMITSU CO., LTD.).

(10) The strength of the coating film was expressed the Young's modulus obtained by "Autograph" (produced by SHIMAZU SEISAKUSHO Co., Ltd.). The Young's modulus was expressed by the ratio of the Young's modulus of the

coating film to that of a commercially available video tape "AV T-120" (produce by VICTOR COMPANY OF JAPAN, LIMITED). The higher the relative value, the more the strength of the coating film is favorable.

(11) The magnetic properties of the magnetic particles and magnetic recording medium were measured under an external magnetic field of 795.8 kA/m (10 kOe) by "Vibration Sample Magnetometer VSM-3S-15 (manufactured by TOEI KOGYO, CO., LTD.)".

(12) The light transmittance is expressed by the linear adsorption coefficient measured by using "UV-Vis Recording Spectrophotometer UV-2100" (manufactured by SHIMAZU SEISAKUSHO, Co. Ltd.). The linear adsorption coefficient is defined by the following formula, and the larger the value, the more the transmittance of light become difficult:

Linear adsorption coefficient (μm^{-1}) = $\{1 - \ln(1/t)\}/FT$
 wherein t represents a light transmittance (-) at $\lambda = 900$ nm, and FT represents thickness (μm) of the coating composition of the film used for the measurement.

As a blank for measuring the linear adsorption coefficient, in case of the non-magnetic substrate composed of the base film and the non-magnetic undercoat layer, the same non-magnetic base film was used, and in case of the magnetic recording medium composed of the base film, the

non-magnetic undercoat layer and the magnetic recording layer, the same non-magnetic base film was used.

(13) The surface resistivity value of a coating film was measured as follows. The coating film to be measured was exposed to an atmosphere kept at a temperature of 25°C and a relative humidity of 60%, for not less than 12 hours. Thereafter, the coating film was slit into 6 mm width, and then placed on metal electrodes each having a width of 6.5 mm such that a coating surface thereof was contacted with the metal electrodes. Two 170-gram weights were fitted to opposite ends of the coating film so as to bring the coating film into close contact with the metal electrodes. Then, a D.C. voltage of 500V was applied between the metal electrodes, thereby measuring a surface resistivity value of the coating film.

(14) The friction coefficient of the magnetic recording medium is expressed by the value obtained from the ratio of a friction force measured between the surface of magnetic tape and metal surface (aluminum mirror surface) using a tensile tester "TENSILON" (manufactured by SHIMADZU SEISAKUSHO Co., Ltd.), to a load applied.

(15) The thickness of each of the base film, the non-magnetic undercoat layer and the magnetic recording layer constituting the magnetic recording medium was measured in the following manner by using "Digital Electronic

Micrometer R351C" (manufactured by ANRITSU CORP.)

The thickness (A) of a base film was first measured. Similarly, the thickness (B) (B = the sum of the thicknesses of the base film and the non-magnetic undercoat layer) of a non-magnetic substrate obtained by forming a non-magnetic undercoat layer on the base film was measured. Furthermore, the thickness (C) (C = the sum of the thicknesses of the base film, the non-magnetic undercoat layer and the magnetic recording layer) of a magnetic recording medium obtained by forming a magnetic recording layer on the non-magnetic substrata was measured. The thickness of the non-magnetic undercoat layer is expressed by $(B) - (A)$, and the thickness of the magnetic recording layer is expressed by $(C) - (B)$.

The results are shown in the Tables 1 to 3.

Table 1 (continued)

Examples	Properties of non-magnetic particles			
	Average major axial diameter (μm)	Average minor axial diameter (μm)	Aspect ratio (-)	Geometrical standard deviation value (-)
Example 1 of our invention	0.145	0.0212	6.8:1	1.38
Experiment 1	0.148	0.0220	6.73:1	1.33

Table 1 (continued)

Examples	Properties of non-magnetic particles		
	BET specific surface area (m^2/g)	Volume resistivity value ($\Omega \cdot \text{cm}$)	Myristic acid absorption (mg/m^2)
Example 1 of our invention	56.3	6.2×10^1	0.21
Experiment 1	52.5	5.6×10^7	0.52

Table 2

Examples	Properties of non-magnetic undercoat layer			
	Thickness (μm)	Gloss (%)	Surface roughness Ra (nm)	Young's modulus (relative value)
Example 1 of our invention	3.5	196	6.6	123
Experiment 1	3.5	193	6.9	118

Table 2 (continued)

Examples	Properties of non-magnetic undercoat layer	
	Linear absorption (μm^{-1})	Surface resistivity value (Ω/cm^2)
Example 1 of our invention	3.44	4.3×10^6
Experiment 1	1.01	7.4×10^{13}

Table 3

Examples	Properties of magnetic recording medium				
	Thickness of magnetic layer (μm)	Coercive force value		Squareness Br/Bm (-)	Gloss (%)
		(kA/m)	(Oe)		
Example 1 of our invention	1.0	155.7	1,956	0.87	212
Experiment 1	1.0	154.9	1,947	0.86	215

Table 3 (continued)

Examples	Properties of magnetic recording medium		
	Surface roughness Ra (nm)	Young's modulus (relative value)	Linear absorption (μm^{-1})
Example 1 of our invention	6.0	127	3.86
Experiment 1	6.2	126	1.12

Table 3 (continued)

Examples	Properties of magnetic recording medium	
	Friction coefficient (μm^{-1})	Surface resistivity value (Ω/cm^2)
Example 1 of our invention	0.21	4.1×10^5
Experiment 1	0.33	3.5×10^{12}

REMARKS

As seen from the above, the non-magnetic particles of Experiment 1 (Example 1 of US Patent No. 5,750,250) have a volume resistivity of $5.6 \times 10^7 \Omega \cdot \text{cm}$. The non-magnetic undercoat layer of Experiment 1 (produced by using the acicular hematite particles obtained in Example 1 of US Patent No. 5,750,250) has a surface resistivity of $7.4 \times 10^{13} \Omega/\text{cm}^2$; and the magnetic recording medium of Experiment 1 (produced by using the acicular hematite particles thereof) has a surface resistivity of $3.5 \times 10^{12} \Omega/\text{cm}^2$, and a friction coefficient of $0.33 \mu\text{m}^{-1}$. Further, the linear adsorption coefficient of the non-magnetic undercoat layer and the magnetic recording medium of Experiment 1 (produced

by using the acicular hematite particles obtained in Example 1 of US Patent No. 5,750,250) is $1.01 \mu\text{m}^{-1}$ and $1.12 \mu\text{m}^{-1}$, respectively.

So, the non-magnetic undercoat layer of Experiment 1 is inferior in surface resistivity and linear adsorption to that of our invention; and the magnetic recording medium of Experiment 1 is inferior in surface resistivity, linear adsorption and the friction coefficient to those of our invention.

6. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: January 19, 2004

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